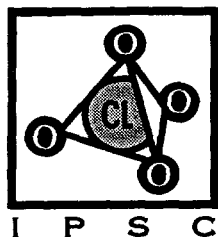


Perchlorate Stakeholders Forum

May 19 - 21, 1998

Henderson, NV

*Sponsored by the
Interagency Perchlorate Steering Committee*



Perchlorate Stakeholders Forum

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May 19-21, 1998 ♦ Henderson, Nevada

Agenda

Day 1: May 19, 1998

7:30 - 8:30 A.M. Registration

8:15 - 8:30 A.M. Administrative Announcements

- Catherine McCracken, Superfund Division, U.S. EPA Region 9, San Francisco, California

8:30 - 9:30 A.M. Keynote Presentations

- William Farland, Director, National Center for Environmental Assessment (NCEA), U.S. EPA
- Thomas W. L. McCall, Jr. Deputy Assistant Secretary, U.S. Air Force (Environment, Safety and Occupational Health)
- Allen Biaggi, Deputy Administrator, Nevada Division of Environmental Protection

9:30 - 12:00 P.M. Session 1 - Background

**9:30 - 10:15 A.M. Overview and History of the Perchlorate Problem,
Time-line for Ongoing Activities on Perchlorate**

- Lt. Col. Dan Rogers, U.S. Air Force, Wright Patterson Air Force Base, Ohio

10:15 - 10:30 A.M. Break

10:30 - 11:00 A.M. Perchlorate Occurrence

- Kevin Mayer, Superfund Division, U.S. EPA Region 9, San Francisco, California
- Brenda Pohlmann, Bureau of Corrective Actions, Nevada Division of Environmental Protection, Las Vegas, Nevada

11:00 - 11:30 A.M. Tribal Concerns Regarding Perchlorate

- Matthew Leivas, Sr., Tribal Council Member and Environmental Assistant, Chemehuevi Indian Tribe, Havasu Lake, California
- Edmond Domingues, Tribal Council Member and Director of Tribal Public Works, Cocopah Indian Tribe, Somerton, Arizona
- Earl Hawes, Project Manager, Quechan Environmental Program, Quechan Indian Tribe, Yuma, Arizona
- Dillon Esquerra, Colorado River Indian Tribes Environmental Protection Office, Colorado River Indian Tribes, Parker, Arizona
- Steve Lopez, Fort Mojave Indian Tribe, Needles, California

- 11:30 - 12:00 P.M. **Facilitated Discussion**
 - **Facilitator: Catherine McCracken, U.S. EPA Region 9**
- 12:00 - 1:15 P.M. **Lunch**
- 1:15 - 5:30 P.M. Session 2 - Perchlorate Health Effects/Toxicity**
- 1:15 - 2:15 P.M. **Background and Objective of Ongoing Studies**
 - **Annie Jarabek, National Center for Environmental Assessment (NCEA), U.S. EPA, Research Triangle Park, North Carolina**
- 2:15 - 2:45 P.M. **Mechanisms of Thyroid Toxicity**
 - **Kevin Crofton, National Health and Environmental Effects Lab (NHEERL), U.S. EPA, Research Triangle Park, North Carolina**
- 2:45 - 3:30 P.M. **Development of Study Protocols, Status of Studies, QA/QC Procedures**
 - **Dave Mattie, Air Force Research Lab, Wright Patterson AFB, Ohio**
- 3:30 - 3:45 P.M. **Break**
- 3:45 - 3:55 P.M. **Development of Revised Reference Dose/Risk Assessment**
 - **Annie Jarabek, NCEA, U.S. EPA**
- 3:55 - 4:15 P.M. **External Peer Review of Risk Assessment**
 - **Peter Grevatt, Office of Solid Waste and Emergency Response (OSWER), U.S. EPA, Washington, D.C.**
- 4:15 - 4:30 P.M. **Update – Office of Water Regulatory and Policy Activities**
 - **Mike Osinski, Office of Water (OW), U.S. EPA, Washington, D.C.**
- 4:30-5:30 P.M. **Facilitated Discussion**
 - **Facilitator: Catherine McCracken, U.S. EPA Region 9**

Day 2: May 20, 1998

- 8:15 - 8:30 A.M. Summary of Previous Day**
- 8:30 - 10:15 A.M. Session 3 - Ecological Impacts/Transport and Transformation**
- 8:30 - 8:55 A.M. **Introduction/Background/Transport and Transformation**
 - **Cornell Long, Human Systems Center, Brooks AFB, Texas**
- 8:55 - 9:20 A.M. **Historical Studies/Applicability**
 - **Ron Porter, Human Systems Center, Brooks AFB, Texas**
- 9:20 - 9:45 A.M. **Proposed Activities - Data Gaps/Future Direction**
 - **Mark Sprenger, Environmental Response Team Center, U.S. EPA, Edison, New Jersey**

9:45-10:15 A.M. **Facilitated Discussion**
- **Facilitator: Carmen White, Superfund Division, U.S. EPA Region 9, San Francisco, California**

10:15 - 10:30 A.M. **Break**

10:30 - 2:15 P.M. Session 4 -Analytical Methods

10:30 -10:45 A.M. **Background on Analytical Techniques and Pending Interlab Study**
- **Stephen Pia, National Environmental Research Lab (NERL), Las Vegas, Nevada**

10:45 -11:30 A.M. **Analysis of Perchlorate by Ion Chromatography (IC)**
- **Howard Okamoto, California Department of Health Services (CA DHS), Berkeley, California**

11:30 -12:15 P.M. **Improved IC Method for Low Level Perchlorate Analysis**
- **Peter Jackson, Dionex Corporation, Sunnyvale, California**

12:15 -1:30 P.M. **Lunch**

1:30 -2:15 P.M. **Facilitated Discussion**
- **Facilitator: Carmen White, U.S. EPA Region 9**

2:15 - 5:00 P.M. Session 5 - Treatment Technology

2:15 - 2:30 P.M. **Background**
- **Ed Urbansky, National Risk Management Research Lab (NRMRL), U.S. EPA, Cincinnati, Ohio**

2:30 - 2:45 P.M. **Introduction to Past and Current Treatment Studies**
- **Wayne Praskins, Superfund Division, U.S. EPA Region 9, San Francisco, California**

2:45 - 3:00 P.M. **Biological Treatment of Wastewater**
- **Jim Hurley, Air Force Research Lab, Tyndall AFB, Florida**

3:00 - 3:15 P.M. **Biological Treatment of Low Level Perchlorate Contamination**
- **John Catts, Baldwin Park Operable Unit Steering Committee, Baldwin Park, California**

3:15 - 3:30 P.M. **Break**

3:30 - 3:45 P.M. **Perchlorate Treatment by Ion Exchange**
- **Rick Sase, Main San Gabriel Basin Watermaster, Azusa, California**

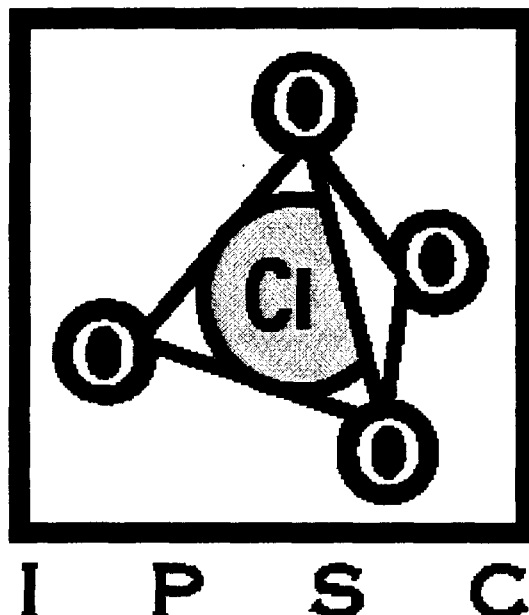
3:45- 4:00 P.M. **Perchlorate Treatment by Enhanced Coagulation and Advanced Oxidation Membranes**
- **Jeanne Marie Bruno, Metropolitan Water District of Southern California, La Verne, California**

- 4:00 - 4:15 P.M. **Future Treatment Studies**
- Frank Blaha, American Water Works Association Research Foundation, Denver, Colorado
- 4:15 - 5:00 P.M. **Facilitated Discussion**
- Facilitator: Andrew Bain, Superfund Division, U.S. EPA Region 9, San Francisco, California
- 7:00 - 9:00 P.M. **Public Availability Session**
- Facilitator: Carmen White, U.S. EPA Region 9

Day 3: May 21, 1998

- 8:30 - 12:00 P.M. **Session 6 - Summary, Next Steps**
- 8:30 - 9:30 A.M. Summary of Discussions from Days 1 & 2
- 9:30 - 11:30 A.M. **Facilitated Panel/Audience Discussion**
- IPSC Steering Committee
- Facilitator: Andrew Bain, U.S. EPA Region 9
- 11:30 - 12:00 P.M. Wrap-up, Next Steps, Time-Line
- 1:30 - 3:30 P.M. Interagency Perchlorate Steering Committee Meeting

DISCUSSION PAPERS FOR THE
PERCHLORATE STAKEHOLDERS
FORUM



May 19-21, 1998
Henderson, Nevada

MEMBERS AS OF MAY 1998

ENVIRONMENTAL PROTECTION AGENCY, DEPARTMENT OF DEFENSE, AGENCY FOR TOXIC SUBSTANCES AND DISEASE REGISTRY

NATIONAL INSTITUTE FOR ENVIRONMENTAL HEALTH SCIENCES, CALIFORNIA DEPARTMENT OF HEALTH SERVICES

NEVADA DIVISION OF ENVIRONMENTAL PROTECTION, UTAH DEPARTMENT OF ENVIRONMENTAL QUALITY

COCOPAH INDIAN TRIBE, COLORADO RIVER INDIAN TRIBES (CRIT), FT. MOJAVE INDIAN TRIBE

CHEMEHUEVI INDIAN TRIBE, QUECHAN INDIAN TRIBE

PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Overview of Perchlorate Issues

Background

Perchlorate anion (ClO_4^-) originates as a contaminant in the environment from the solid salts of ammonium, potassium, or sodium perchlorate. Perchlorate salts are quite soluble in water. The resultant anion (ClO_4^-) is exceedingly mobile in aqueous systems and can persist for many decades under typical groundwater and surface water conditions, due to kinetic barriers to its reactivity with other available constituents. Ammonium perchlorate is manufactured for use as an oxidizer component in solid propellant for rockets, missiles, and fireworks. Because of its shelf life, it must be periodically washed out of the country's missile and rocket inventory and replaced with a fresh supply. Thus, large volumes of the compound have been disposed of in Nevada, California, Utah, and likely other states, since the 1950's. Ammonium perchlorate is also used in certain munitions, fireworks, the manufacture of matches, and in analytical chemistry.

Potassium perchlorate had, until recently, been used therapeutically to treat hyperthyroidism resulting from an autoimmune condition known as Graves' disease. Potassium perchlorate is still used diagnostically to test thyroid hormone (TSH, T3 and T4) production in some clinical settings. The basis for the effect on thyroid hormone function is the competitive inhibition of iodide anion uptake by perchlorate which results in reduced thyroid hormone production. Thyroid hormone deficiencies can affect normal metabolism, growth and development. The limited database on the toxicology of perchlorate confirms its potential to disrupt thyroid hormone production in mammalian test species, but no robust data exist to evaluate the dose-response for this thyroid effect or to evaluate other potential target tissues or effects. There are no existing data to evaluate the effects of perchlorate in potentially susceptible population such as developing fetuses or to evaluate its effects on ecological systems. Studies are now underway to evaluate these potential effects.

Issues

Perchlorate is of concern because of the existing uncertainties in (1) the toxicological database documenting its health effects at low levels in drinking water; (2) the actual extent of the occurrence of perchlorate in ground and surface waters, which is compounded by some uncertainty in the validation of the analytical detection method; (3) the efficacy of different treatment technologies for various water uses such as drinking water or agricultural application;

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and (4) the extent and nature of ecological impact or transport and transformation phenomena in various environmental media.

This background discussion paper will provide you with general information and how plans are underway to integrate all the new information from a variety of areas in order to characterize the potential risk that perchlorate contamination may pose. Additional discussion papers will provide you with more in-depth information on these areas, including: (1) development of reliable analytical methods to detect perchlorate; (2) where perchlorate has been found; (3) the assessment of the health effects and toxicology studies to derive a benchmark value by which to evaluate risk; (4) research underway to evaluate the ecological impacts; and (5) development of treatment technologies to address various water uses.

Where Perchlorate Contamination Occurs

Within several months following the April 1997 development of a low level detection methodology, perchlorate had been discovered at various manufacturing sites and in well-water and the drinking water supplies in California, Nevada, and Utah. At this time, there has not been a systematic national survey of perchlorate occurrence. Only a relatively small number of water supplies have been monitored using the more sensitive method, primarily in the western states with a few sample results now available in the south.

The majority of locations where perchlorate has been detected in the groundwater are in California, associated with twelve facilities which have manufactured or tested solid rocket fuels for the Department of Defense (DoD) or the National Aeronautics and Space Administration (NASA). Two facilities which manufactured ammonium perchlorate in Nevada were found to have released perchlorate to groundwater which is the source for low levels (4 to 16 ppb) in Lake Mead and the Colorado River. This water is used for drinking water supply, irrigation and recreation for millions of people in Nevada, California, Arizona, and Native American Tribes. Other releases have been detected in Utah and Texas.

Information on other potential sites across the country is being gathered from DoD and NASA searches and from U.S. Environmental Protection Agency (EPA) information requests made to perchlorate manufacturers. Initial records indicate that perchlorate has been shipped to facilities in 37 states. EPA has notified State, Tribal, and local governments when it has evidence of perchlorate manufacture and use in their jurisdictions.

Interagency Perchlorate Steering Committee (IPSC)

An Interagency Perchlorate Steering Committee (IPSC) was formed in January 1998 to bring together government representatives from the EPA, DoD, Agency for Toxic Substances and Disease Registry (ATSDR), National Institute for Environmental Health Sciences (NIEHS), and

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affected State, Tribal, and local governments. Participation in the IPSC has also been solicited from other governmental entities.

The charter of the IPSC is to facilitate and coordinate accurate accounts of related technological issues (occurrence, health effects, treatability and waste stream handling, analytical detection, and ecological impacts) and to create information transfer links for interagency and intergovernmental activities regarding these areas of concern.

The IPSC recently collaborated with EPA's Office of Research and Development (ORD) on a report to a Congressional House committee that assesses the state-of-the-science on the health effects of perchlorate on humans and the environment and the extent of perchlorate contamination. The report also contained recommendations for future research to address emerging issues.

Monthly teleconferences are held to update participants on events and breaking news regarding controversial or technological issues. Public meetings, such as the May 1998 meeting in Henderson, Nevada, will be held to distribute the most current scientific information on the key issues and to hear stakeholder and public concerns.

An Integrated Approach to Risk Characterization: Current Activities

A number of key pieces of information are necessary to characterize the risk of perchlorate contamination in order to formulate appropriate management strategies to mitigate potential risk. Accurate characterization of exposures rely on reliable analytical detection methods. The exposure estimates can not be gauged with respect to their risk unless a robust health risk estimate is available. Treatment technologies should be targeted to levels of concern and tailored to the intended use of the water. Research to obtain additional data and development of new methods or applications are underway in most of these areas to ensure that the state-of-the-science is brought to bear on addressing the unique issues of perchlorate contamination. Technology transfer is necessary so that all affected parties and concerned citizens are apprised of accurate and reliable information that is up to date with the evolving state-of-the-science.

Reliable Analytical Methods

As noted above, the first critical data needed for a comprehensive risk characterization is accurate information on occurrence: where the contamination occurs, the nature (type) and extent (magnitude) of the exposure. Occurrence survey studies require a reliable and accurate analytical method for detecting perchlorate in drinking water and various aquifer types or other environmental media (e.g., irrigated food crops). Ion chromatography (IC) is the state-of-the-art technology for analysis because historical methods based on gravimetry, spectrophotometry, or atomic absorption are non-specific for perchlorate. There are several existing IC methods, including the recent analytical method developed by the California Department of Health

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Services (CA DHS), Dionex, and one developed by the Air Force Research Laboratory/Operational Toxicology Branch (AFRL/HEST). These methods depend upon retention time in a standard to identify any peak with the same or similar retention time as perchlorate in a water sample. The robustness of existing IC methods for the analysis of perchlorate in water with high total dissolved solids has been questioned. Research is underway that will evaluate the variability, reproducibility, accuracy and precision of the IC methods across laboratories and to determine the appropriate concentration ranges for measurement.

Health Effects Assessment

The second critical piece of information is to have a comprehensive health effects evaluation that can serve as the basis for development of exposure guidance levels. The toxicology data available to evaluate the potential health effects of perchlorate are extremely limited. The EPA Superfund Technical Support Center issued a provisional reference dose (RfD) in 1992 and a revised provisional RfD in 1995. The provisional RfD values (1992 and 1995) were based on an acute study in which single doses of potassium perchlorate caused the release of iodide from the thyroids of patients with Graves' Disease. Uncertainty factors that ranged from 300 to 1000 were applied to account for missing endpoints and extrapolations required to calculate a lifetime human exposure level. Standard assumptions for ingestion rate and body weight were then applied to the RfD to calculate the reported range in the ground water cleanup guidance levels of 4 -18 parts per billion (ppb). The CA DHS adopted 18 ppb as its provisional action level. An RfD is calculated as an estimate of a daily human exposure that will result in no deleterious noncancer effects over a lifetime. Ideally, an RfD is based on a database that evaluates an array of endpoints that address potential toxicity during various critical lifestages, from developing fetus through adult and reproductive stages. New studies were begun in 1997 and are underway to provide data on these missing endpoints. Additional new studies will also provide data to evaluate the potential for cancer risk. The National Center for Environmental Assessment (NCEA) in the Office of Research and Development (ORD) of the EPA plans to evaluate these new data and issue a new assessment with a revised RfD at the end of September 1998. The new assessment, all the new data and the study protocols will then be subjected to an external peer review in October 1998 before the assessment is finalized.

Ecological Impact Assessment / Transport and Transformation

Another potential area of health impact is on ecosystems and via indirect exposure pathways (e.g., agriculture or fishing). Searches of available databases have revealed minimal information on the ecological effects of ammonium perchlorate or any of its other salts. Essentially no reliable data exist for its effects on various soil, sediment or aquatic receptors including: aquatic vertebrates, aquatic or sediment invertebrates, bacteria or plants. Approaches for the evaluation of effects on ecological receptors is complicated by the lack of data on its environmental transport and transformation processes. These include data on the effects of soil chemistry (soil composition, adsorption processes, particle size and water saturation, complexation behavior with humic and fulvic materials, pH, etc.), movement characteristics in various media, adsorption to soils of high and low cation and anion exchange capacity, and the effect of ammonia. Development of predictive environmental transport and transformation

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models would be useful both to assessing ecological impact as well as directing sampling strategies to determine occurrence monitoring sites. Research has been recommended to develop data on the effects of perchlorate on various ecological receptors and the various parameters needed to develop reliable transport and transportation models that can forecast the fate of perchlorate in various aquifer types and environmental media.

Treatment Technologies

The health estimate such as the oral RfD is typically compared against the exposure estimates to characterize potential health risks. Such a comparison will also target the levels to which reliable treatment technologies must be developed. Perchlorate is very unreactive towards most reducing agents when cold and dilute and has low reactivity as an oxidant due to kinetic barriers. These same properties make developing treatment technologies difficult, especially at low concentration levels. No one technology or process will likely provide an effective solution for every occurrence of perchlorate contamination in water supplies due to a large number of independent variables. Different technology may also be developed depending upon the intended use of the treated water (e.g., drinking water versus agricultural application). Treatment technologies and processes have been developed by industry and the Air Force Research Laboratory, Materials and Manufacturing Directorate (AFRL/MLQE) to recover perchlorate for reuse and to treat residual wastewater containing high concentrations of perchlorate, i.e. 500-10,000 parts per million (ppm), from the manufacture and maintenance of rocket motors. Research is underway to develop technologies that meet the new challenge of treating low-concentration (5 ppb to 500 ppm) perchlorate contamination present in ground and surface water supplies.

EPA's Future Regulatory Plans:

The Safe Drinking Water Act (SDWA), enacted by Congress in 1974 and amended in 1986 and 1996, provides the basis for safeguarding public drinking water systems from contaminants that pose a threat to public health. The purpose of SDWA is to protect public health by ensuring that public drinking water systems provided tap water that is safe for drinking and bathing. Within EPA, the Office of Ground Water and Drinking Water (OGWDW) develops National Primary Drinking Water Regulations (NPDWR) to control the levels contaminants that may occur in public drinking water systems.

The 1996 amendments to the SDWA require EPA to publish a list of contaminants that are not currently subject to a NPDWR and are known or anticipated to occur in public water systems. This list, known as the Contaminant Candidate List (CCL), will be the source of priority contaminants for research, guidance development, and selection of contaminants for making regulatory determinations and/or monitoring by the States. The SDWA requires EPA to make a determination of whether or not to regulate not less than 5 contaminants from the CCL by 2001. The CCL must also be reviewed and updated every 5 years, or again in 2003.

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With broad public input and consultation with the scientific community, a draft CCL was published on October 6, 1997. The draft CCL specifically requested comment on whether to include perchlorate on the CCL based on the limited information EPA had received on its occurrence in drinking water supplies at the time of publication. As a result of the public comments and additional occurrence information obtained, the Agency determined that sufficient information exists to raise concern over perchlorate's potential public health impact, and it was added to the final CCL published on March 2, 1998.

The CCL consists of 50 chemical and 10 microbiological contaminants and is divided into two categories: (1) contaminants for which sufficient information exists to begin to make regulatory determinations by 2001, and (2) contaminants for which additional research and occurrence information is necessary before regulatory determinations can be made. Perchlorate is identified as a contaminant needing additional research in the areas of health effects, treatment technologies, analytical methods, and more complete occurrence data.

State Regulatory Plans:

In 1997, the CA DHS and California EPA's Office of Environmental Health Hazard Assessment reviewed the EPA risk assessment reports for perchlorate. As a result, California established its action level of 18 ppb. Perchlorate concentrations lower than 18 ppb are not considered to pose a health concern for the public, including children and pregnant women. CA DHS advises water utilities to remove drinking water supplies from service if they exceed the 18 ppb action level. If the contaminated source is not removed from service due to system demands and if drinking water that is provided by the utility exceeds the action level, CA DHS will advise the utility to arrange for public notification to its customers. On August 1, 1997, CA DHS informed drinking water utilities of its intention to develop a regulation to require monitoring for perchlorate as an unregulated chemical. Legislative action to establish a state drinking water standard for perchlorate has been introduced but has not been brought to a vote (CA Senate Bill 1033).

The Nevada Division of Environmental Protection (NDEP) has authority under Nevada Water Pollution Control Regulations to address pollutants in soil or groundwater that pose a threat to the waters of the state. The State's Corrective Action Regulations direct NDEP to establish Action Levels for hazardous substances, pollutants or contaminants using drinking water standards (MCLs), background levels or protective levels (determined by IRIS or equivalent). In August, 1997, Nevada determined that the health-based action level of 18 ppb, as established in California, would be the recommended action level for cleanup pending a more current risk assessment.

No other state is known to have adopted action levels for perchlorate primarily since levels greater than 18 ppb have not been found in water supplies in other States.

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Technology Transfer and Public Outreach

Accurate information and communication tools are needed to keep the general public, water utilities and their customers informed regarding the state-of-the-science and important issues related to perchlorate toxicity, including: analytical detection methods, occurrence, treatment technologies, ecological impact, and environmental transfer and transformation.

Bringing effective water treatment technologies to bear on perchlorate contaminated drinking water quickly and affordably is one of the primary goals of technology transfer. This requires emphasis on two important factors in the rapid development and implementation of new technologies. First, information regarding technology development and application activities should be disseminated to the widest possible audience. The IPSC will continue to collect and disseminate information regarding treatment technologies and remain involved in facilitating research and technology demonstration efforts. Effective tools that reach a broad spectrum of the public, such as discussion papers, teleconferences, an updated Web page, and news releases have been developed. Subcommittees of the IPSC are been charged with developing and updating discussion papers. EPA's Office of Water (OW) is developing a website with links to the Office of Solid Waste and Emergency Response (OSWER) and the National Center for Environmental Assessment (NCEA). EPA regional offices have been working with State authorities on news releases.

Second, drinking water authorities and purveyors of drinking water treatment technologies need to be involved as partners in research and technology demonstration. The IPSC will again serve to coordinate these activities as required. Attention to these key technology transfer issues will ensure that sound treatment strategies are developed and implemented which are responsive to the unique requirements of each affected area.

PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Occurrence

Introduction

Nearly all of the sources of perchlorate in the environment discovered to date were identified following the recent (March, 1997) development of the methodology to detect dilute concentrations by the California Department of Health Services (DHS). Within six months of this analytical advance, perchlorate was found at various manufacturing sites and in some wells and drinking water supplies of communities in California, Nevada, and Utah. At this time, there has not been a systematic national survey of perchlorate occurrence. Only a relatively small number of water supplies have been monitored using the more sensitive method, primarily in the western States, with a few sample results now available in other regions of the US. As more laboratories across the country adopt improved analytical methods, it is likely that other sources will be identified.

Identification of the magnitude and extent of perchlorate occurrence in the environment is important in assessing the routes of exposure to humans and determining the different types of organisms and ecosystems that may be affected. Further search for possible sources of perchlorate contamination is essential for alerting States and communities and to assess the need to develop national policies or regulations.

Where Perchlorate Contamination Occurs

The majority of locations where perchlorate has been detected in groundwater are in California, associated with twelve facilities which have manufactured or tested solid rocket fuels for the military or National Aeronautics and Space Administration (NASA). Seven National Priority List sites (federal Superfund sites) in California are affected by these releases. Two facilities which manufactured ammonium perchlorate near Henderson, Nevada, were found to have released perchlorate to groundwater. Perchlorate from the Henderson area has entered the surface water and has been detected at low levels (4 to 16 ppb) in Lake Mead and the Colorado River. This water is used as a drinking water supply for more than 1 million people in Nevada, over 10 million in southern California and more than a million in Arizona. Native American Tribes and other communities along the Colorado River rely on the water for irrigation and recreation.

Perchlorate entered a private water supply well in Utah from contamination on the property of a rocket motor manufacturer near Magna, west of Salt Lake City. A storm drain from a perchlorate-handling area of the Longhorn Army Ammunition Plant in northeast Texas was discovered discharging detectable levels of perchlorate to Caddo Lake.

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The concentrations reported in wells and surface water vary widely. At one facility near Henderson NV, perchlorate in groundwater monitoring wells was measured as high as 0.37% (37 million parts per billion). Water suppliers in northern and southern California have detected perchlorate in 110 public water supply wells, with 33 of these having perchlorate greater than 18 ppb, which is the current action level in California. The highest level of perchlorate reported in any water supply well was 280 ppb with few others greater than 100 ppb.

The American Water Works Service Company recently completed sampling and analysis of 425 drinking water supply wells in 16 States. Of these, 7 wells (1.6%) were found with perchlorate above 4ppb, with the highest level at 6.4ppb. The wells testing positive for perchlorate were located in CA, IN, IA, and PA. Drinking water wells in the following States had no detections of perchlorate: AZ, CT, IL, MD, MA, MI, MO, NJ, NM, NY, OH, and WV.

Information on other potential sites across the country is being gathered from the Department of Defense (DoD) and NASA searches and from U.S. Environmental Protection Agency (EPA) information requests made to perchlorate manufacturers. About 90% of the perchlorate produced by major US manufacturers has been shipped for use as a rocket fuel oxidizer, with most of the remainder used in explosives. Initial records indicate that perchlorate has been shipped to facilities in 37 States. EPA has notified State, Tribal and local governments when it has evidence of perchlorate manufacture and use in their jurisdictions. The American Water Works Association Research Foundation (AWWARF) is coordinating a survey to characterize possible perchlorate contamination of drinking water sources in areas of high risk. EPA will build upon these survey data and other information in order to discover potential sources and evaluate threats to water resources.

Questions for Discussion

1. How might various State and federal agencies enhance coordination in searching for perchlorate contamination around the US?
2. What additional sources of contamination might be discovered?
3. What criteria should be used to design a broader based survey of perchlorate occurrence?
4. Are there concerns for perchlorate contamination outside the US?

PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Health Effects / Toxicology of Perchlorate

Introduction

A significant portion of the expedited research underway to address perchlorate contamination in the environment has been dedicated to obtaining a reliable and comprehensive data base on the health effects and toxicology of perchlorate. Such robust data are necessary to develop a health risk assessment that includes an estimate called a reference dose (RfD) which can be used to evaluate the potential risk of human exposures. The RfD can also be used in risk management programs to help guide the range where analytical methods must be effective and to target treatment technologies. The health effects data serve as the lynchpin in the overall integrated approach to addressing the emerging issues of perchlorate contamination.

Background

The currently available database on the health effects and toxicology of perchlorate or its salts is very limited. The majority of human data are clinical reports of patients treated with potassium perchlorate for hyperthyroidism resulting from an autoimmune condition known as Graves' disease. Potassium perchlorate is still used diagnostically to test thyroid hormone [thyroid stimulating hormone (TSH), triiodothyronine (T3), and thyroxine (T4)] production in some clinical settings. The basis for the effect on thyroid hormone function is the competitive inhibition of iodide anion uptake into the thyroid gland by perchlorate anion (ClO_4^-) which then results in reduced thyroid hormone production.

It is difficult to establish a dose-response for the effects on thyroid function from daily or repeated exposures in normal humans from the data on patients with Graves' disease because of a variety of confounding factors, including: the effect of the disease, that often only a single exposure and not repeated exposures were tested, that only one or two doses were employed, and that often the only effect monitored was iodine release from the thyroid or control of the hyperthyroid state. There are limited data in normal human subjects and laboratory animals that support the effect of perchlorate on thyroid hormones, but the majority of these additional studies suffer from the same limitations with respect to the number of doses and exposures. These limitations prevent establishment of a quantitative dose-response estimate for the effects on thyroid hormones after long-term repeated exposures to perchlorate in healthy human subjects.

The typical objective of a health risk assessment is to evaluate a comprehensive array of testing endpoints that represent various life stages in which potential effects could occur, e.g., the developing fetus through adult and for effects on reproductive capability. Thyroid hormone deficiencies, such as those induced by perchlorate, can affect normal metabolism, growth and development. No robust data exist to evaluate other potential target tissues or effects. There are no data to evaluate the effects of perchlorate in potentially susceptible population such as

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developing fetuses, nor are there data on the effects of perchlorate on reproductive capacity of male or female laboratory animals.

Benign tumors have been reported in the thyroids of male Wistar rats and female BALB/c mice treated with repeated, high dose exposures (2 years at 1,339 and 46 weeks at 2,147 mg/Kg-day, respectively) of potassium perchlorate in drinking water. Benign tumors in the thyroid have been established to be the result of a series of progressive changes that occur in the thyroid in response to interference with thyroid-pituitary homeostasis (i.e., perturbation of the normal stable state of the hormones and functions shared between these two related glands). This progression is similar regardless of the cause of the thyroid hormone interference (Hill et al., 1989; Capen, 1997; Hurley et al., submitted). The EPA has adopted the policy that an assumption of a threshold based on these precursor lesions along the progression is appropriate for the dose-response of chemicals which cause this type of disruption in the thyroid when they do not have genotoxic activity, i.e., cause damage to DNA or show other genetic disruption (U.S. EPA, 1998). Therefore, a dose-response estimate established using the no-observed-adverse-effect level for the precursor lesions should be an estimate also protective for potential benign tumor development. Existing shorter-term studies indicate that perchlorate causes changes in the thyroid typical of the progression described and genotoxic studies are underway to establish that perchlorate does not have any activity relevant to carcinogenicity.

Provisional Health Risk Assessment

The EPA Superfund Technical Support Center issued a provisional reference dose (RfD) in 1992 and a revised provisional RfD in 1995. An RfD is calculated as an estimate of a daily oral human exposure that will result in no deleterious noncancer effects over a lifetime. Ideally, an RfD is based on a database that evaluates an array of endpoints that address potential toxicity during various critical lifestages, from developing fetus through adult and reproductive stages. The provisional RfD values (1992 and 1995) were based on an acute study in which single doses of potassium perchlorate caused the release of iodide from the thyroids of patients with Graves' Disease. The no-observed-adverse-effect-level (NOAEL) was determined to be 0.14 mg/Kg-day based on release of iodine in the thyroid followed by incomplete inhibition of iodine uptake. Uncertainty factors that ranged from 300 to 1000 were applied to account for data missing on additional endpoints and extrapolations required to calculate a lifetime human exposure level. Standard assumptions for ingestion rate and body weight were then applied to the RfD to calculate the reported range in the ground water cleanup guidance levels of 4 -18 parts per billion (ppb). The California Department of Health Services (CA DHS) adopted 18 ppb as its provisional action level.

The provisional RfD values issued are listed by the EPA only as provisional because they did not undergo the internal Agency and external peer review required of estimates available on the EPA's Integrated Risk Information System (IRIS). The outcome of an external peer review convened in March 1997 of an analogous RfD derivation by an independent organization, Toxicology Excellence for Risk Assessment (TERA), was the determination that the health effects and toxicity data were insufficient for a credible quantitative risk analysis. The external peer review panel concluded that the data were not sufficient to rule out effects of perchlorate on other organs, so that it could not be determined unequivocally that the effects on the thyroid were the critical effect. In particular, the reviewers were concerned that developmental toxicity,

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notably neurological development due to hypothyroidism during pregnancy, could be a critical effect of perchlorate that has not been adequately examined in studies to date.

New Health Effects / Toxicology Studies Underway

In response to the March 1997 external peer review of the provisional RfD value, a subsequent external peer review of experts was convened in May 1997 to recommend and prioritize a set of studies to address the key data gaps and reduce uncertainties in various extrapolations. The objective of the new studies is to provide a comprehensive database that provides for development of a robust RfD estimate that reduces the uncertainties inherent in the provisional values. Funding for the studies was procured and obligated through a variety of sources, principally the USAF and the Perchlorate Study Group (PSG).¹ The protocols for the studies were reviewed by external peer reviewers from the EPA, California EPA, academia, industry, private institutes and Health Canada. The timeframe for the development of these new data has been precedent setting and has been a direct result of a unique partnering initiative. Typical research and development mechanisms would have required a number of years to accomplish these same studies.

Eight new studies were recommended in order to provide a comprehensive array of endpoints. These are described below along with their anticipated role in informing the revised health risk assessment.

(1) 90-Day Subchronic Oral Bioassay Study. This study is considered the minimum data requirement for derivation of an oral RfD. The study will identify other target tissues, test young adult rats, and also provide data on the effect of repeated exposure to perchlorate on thyroid hormone levels. These data may also allow reduction of the uncertainty factor applied for database deficiencies.

(2) Neurobehavioral Developmental Study. This study will evaluate the potential for developmental neurotoxicity of perchlorate by assessing functional and morphological endpoints in offspring from mother exposed during pregnancy and lactation. Neurotoxicity endpoints may be a critical effect and the developing organism a sensitive subpopulation. These data may allow reduction of the uncertainty factors applied for intrahuman variability and database deficiencies.

(3) Segment II Developmental Study. This study will evaluate the potential for perchlorate to cause birth defects in rabbits and will identify a potentially critical effect and subpopulation. This study will also provide data on the thyroid hormone effects in a second species (in addition to rats). These data may allow reduction of the uncertainty factor applied for database deficiencies.

¹The PSG is a consortium of defense contractors and manufacturers including: Alliant Techsystems, American Pacific/Western Electrochemical Company, Atlantic Research Corporation, Lockheed Martin, Thiokol Propulsion Group, and United Technologies Chemical Systems.

(4) Two-Generation Reproductive Toxicity Study. This study will evaluate the potential for perchlorate to cause deficits in reproductive performance in adult rats and for toxicity in the young offspring. This study may identify a potentially critical effect and allow for reduction of the uncertainty factor applied for database deficiencies.

(5) ADME (Absorption, Distribution, Metabolism, and Elimination) Studies. These studies will be performed to understand the pharmacokinetics (how perchlorate is absorbed, distributed, metabolized and excreted) of perchlorate in test animals and humans. These data will provide information that will allow construction of quantitative extrapolation of dose across species (e.g., rat to human).

(6) Perchlorate Mechanism Studies. These studies will be conducted by a comparison of the existing literature and of new *in vitro* and *in vivo* data that evaluate the effects of perchlorate on the iodide uptake mechanism across species to aid in the quantitative extrapolation of dose.

(7) Genotoxicity Assays. These studies will evaluate the potential for carcinogenicity by evaluating mutations and toxic effects on DNA. These data will be useful to evaluate whether the benign thyroid tumors are likely to be a result of the proposed threshold pathogenesis process.

(8) Immunotoxicity Studies. These studies will evaluate the potential for perchlorate to disrupt immune function and identify a potentially critical effect. These data may help to reduce the uncertainty factor applied for database deficiencies.

Additional work may be required to mathematically model the dosimetry (pharmacokinetics) and toxic effects in order to increase the accuracy of a health risk determination, but this will need to be evaluated as the new data become available. An epidemiological study has been proposed to look at infant thyroid hormone data from mothers who were exposed in their drinking water supplies. The analysis would rely on the dose reconstruction data to the level of either a city or census block and will assume either that all women who lived in that area were exposed to that level of perchlorate or impose standard assumptions from other such studies (e.g., 20% of women drink bottled water). The dose reconstruction of what was in the water would have to be constructed on occurrence data once the hydrology in the aquifers and transport and transformation processes can be worked out. Both of these studies are considered refinements to the revision of the RfD that will likely result from the new studies.

EPA Plans for Revised Health Assessment and Peer Review

Revised Health Risk Assessment

The National Center for Environmental Assessment (NCEA) in the Office of Research and Development (ORD) of the EPA plans to evaluate the health effects and toxicology data from these new studies and then issue a new assessment at the end of September 1998. The new assessment, all the new data, and the study protocols will then be subjected to an external peer

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review in October 1998 before the assessment is finalized. The assessment, data, and protocols will be available to the public at the time of release to external peer review.

Once finalized, this new peer-reviewed health assessment and new oral RfD will serve as a more robust health effects estimate than the existing provisional values with which to evaluate exposure estimates in order to characterize potential risk from perchlorate contamination or with which to develop guidance levels for cleanup and to target treatment technologies.

External Peer Review of Revised Assessment

Independent, external peer review of the study protocols, toxicity studies, and revised reference dose and health assessment for perchlorate will be critical to ensuring that future decisions based on the RfD will be protective of human health. EPA's Office of Solid Waste and Emergency Response (OSWER) will task a qualified contractor to manage peer review of technical issues related to the development of the reference dose, including study design, conduct of toxicity studies, statistical treatment of data, selection of critical effect, selection of uncertainty factors and risk characterization. The peer review will be conducted by a panel of technical experts in developmental toxicology, reproductive toxicology, genetic toxicology, general toxicology, pathology, biostatistics, dose-response modeling and risk assessment. Peer reviewers will be selected from a pool of candidates nominated by stakeholders in the perchlorate issues. The RfD assessment package, supporting studies, and study protocols for the new data will be distributed to the peer review panel in advance of the peer review meeting. Peer reviewers will independently review the RfD assessment package and supporting studies, and will submit their written comments to OSWER's contractor prior to the peer review meeting. The peer reviewer's comments will be compiled by OSWER's contractor and will be distributed to all of the peer reviewers and the public in advance of the meeting. The peer reviewers will gather for a two day meeting in a location selected based on accessibility to stakeholders and the peer reviewers. The public will be invited to attend and observe the peer review meeting. Following the peer review meeting, the peer review panel will generate a report detailing their comments on the reference dose package and supporting studies. EPA NCEA will generate a responsiveness summary report which will discuss in detail how they will address the comments raised by the peer reviewers. The provisional reference dose will subsequently be issued by EPA.

Questions for Discussion

1. What are the effects of hypothyroidism in adults versus infants?
2. What relevance do these effects have to children's health?
3. What are the potential impacts to pregnant women who drink contaminated water?
4. How will new information on health effects be used in the future?

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Ecological Effects/Transport and Transformation

Background

Perchlorate salts are quite soluble in water. The resultant anion (ClO_4^-) is exceedingly mobile in aqueous systems and can persist for many decades under typical groundwater and surface water conditions, due to kinetic barriers to its reactivity with other available constituents. This mobility and persistence may pose a threat to ecological receptors and whole ecosystems, either by direct harm to organisms, or it may indirectly affect their ability to survive and reproduce.

Currently, there are no data to evaluate the effects of perchlorate on ecological systems nor is there data about the possible uptake of perchlorate into agricultural products through irrigation of the food crops. Analytical tests have been derived to detect perchlorate in water, but little is known about testing food crops for perchlorate.

This fact sheet will describe historical studies of perchlorate on non-human receptors. Next, it will present tests proposed by the U.S. Environmental Protection Agency (EPA) and the U.S. Air Force (USAF) to address the current gaps in knowledge. The information gained from these screening-level tests will be used to support recommendations for further studies. Lastly, this fact sheet will outline the effort by the USAF to determine fate and transport of ammonium perchlorate in the environment.

Historical Studies

Searches of available databases have revealed minimal information on the ecological effects of ammonium perchlorate or any of its other salts. Little data exist to describe its effects on various soil, sediment or aquatic receptors including: aquatic vertebrates, aquatic or sediment invertebrates, bacteria or plants. The data that is available suggest effects on thyroid-hormone mediated development in the South African clawed frog, *Xenopus laevis* in the range of 50-100 parts per million (ppm); and 1000 ppm in recent studies has been shown to completely block the metamorphosis of tadpoles. Effects on development and population growth have also been indicated in the freshwater sea lamprey at 100 ppm and the freshwater hydra at 350 ppm. Mortality was observed in cold water trout (6000-7000 ppm) and *Daphnia magna* (670 ppm). Effects on seed germination and growth of agricultural plants were reported at 10 ppm.

Proposed Activities

The USAF/Detachment 1, Human Systems Center, Brooks AFB, in conjunction with EPA, has developed a proposal for a battery of screening level bioassays in laboratory-reared organisms representative of ecological receptors across soil, sediment, and water column receptors to evaluate dose-response relationships. The identified tests focus on identifying gross (direct) toxicity tests whose endpoints can include mortality, growth, and reproductive success. Dose response relationships can be evaluated.

In general, the tools used to evaluate chemical effects on soil and benthic invertebrates, plants, and fish include benchmark values, toxicity tests, bioaccumulation estimates, and field studies. In the absence of accepted benchmark values, a tiered approach to a toxicity assessment of effects on ecological receptors is suggested. The purpose of a tiered approach is to do necessary and sufficient amount of work to characterize risk to an ecological receptor with an acceptable degree of uncertainty. In this approach to describe ecological impact of perchlorate, Tier 1 included the literature search described under Historical Studies. Tier 2 will include the tests shown below. If significant toxicity is demonstrated in a suite of bioassays more sophisticated assessments can be implemented. Bioassays with standard protocols and general regulatory acceptance were chosen.

Proposed tests include:

Test Organism	Matrix
<i>Daphnia magna</i> or <i>Ceriodaphnia dubia</i>	Sediment invertebrate
<i>Chironomus tentans</i>	Larval sediment invertebrate
<i>Hyallela azteca</i>	Sediment invertebrate
<i>Lemna minor</i> (duckweed)	Vascular plant (aquatic)
Fathead minnow	Aquatic vertebrate
Earthworm	Soil invertebrate
Microtox	bacteria (marine)

Although these are screening level tests and only give us an idea of gross toxicity, they will provide needed dose-response information to make decisions on the need for the next tier of tests (Tier 3) to be completed as required (e.g., bioavailability, bioaccumulation, histopathology, etc.).

Transport and Transformation:

The USAF has begun to determine the transport and transformation (also called fate and transport) of ammonium perchlorate in the environment. This information can be used to predict the flow of perchlorate in the subsurface. Currently, a literature search has been completed which describes fate and transport of ammonium perchlorate in the subsurface. The study

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identifies and assesses factors such as solubility, adsorption, biodegradation, chemical reactions, dispersion, diffusion, and other processes affecting fate and transport of perchlorate.

The literature shows perchlorate to be non-volatile, so inhalation of perchlorate vapor is not expected. However, perchlorate salts do exhibit high solubility in water, which leads to high mobility in surface water and groundwater. Its density is nearly twice that of water, so it will sink in water. Concentrated solutions are also more dense than water. Because perchlorate salts are so soluble, perchlorate ion will predominate in solution. However, potassium is less soluble than ammonium, so it is possible that potassium perchlorate may precipitate ("salt-out") of solution, decreasing migration.

Perchlorate is a kinetically stable ion, which means that reduction of the chlorine atom from a +7 oxidation state in perchlorate to a -1 oxidation state as a chloride ion does not occur spontaneously—it would require an input of energy (e.g., heat or light) or the presence of a catalyst to help the reaction occur.

Dilution and precipitation reactions are presumed to have the most significant effect on perchlorate migration. Through dilution, concentrations would be expected to be significantly less away from the source. Precipitation, can help decrease mobility of perchlorate, but the salt can then re-dissolve, be transported, and precipitate repeatedly. Sorption is not expected to attenuate perchlorate since it absorbs weakly to most soil minerals. Since perchlorate is chemically stable, natural chemical reduction in the environment is not expected to be significant. The treatment technology subcommittee of the Interagency Perchlorate Steering Committee (IPSC) is examining biological reduction of perchlorate.

Based on the information gathered in this literature review, recommendations have been made for a second phase to fill many of the gaps in the current understanding of perchlorate transport and transformation. This will help develop models to predict and describe perchlorate migration in the subsurface.

Questions for Discussion

1. Do plants uptake the perchlorate ion when irrigated with perchlorate-containing water?
2. What tests can be used to determine if perchlorate is in the food crop?
3. Are there other ecological species that should be considered for potential effects from perchlorate?

PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Analytical Methods

Introduction

In January of 1997, the California Department of Health Services' Division of Drinking Water and Environmental Management requested the Sanitation and Radiation Laboratory Branch (SRLB) to test for perchlorate in drinking water wells potentially affected by groundwater migrating from the Aerojet facility near Sacramento. Existing U.S. Environmental Protection Agency (EPA) risk assessment studies on perchlorate indicated that a reporting limit of at least 4 parts per billion (ppb) would be necessary. No procedures were available for measuring perchlorate at such low levels. An Ion Chromatographic (IC) method was capable of detecting 400 ppb and during the previous year Aerojet had improved the method to detect 100 ppb. By March 1997, SRLB and an analytical equipment manufacturer had developed an IC method that achieved a method detection limit of approximately 1 ppb and a reporting limit of 4 ppb. This method was used to detect perchlorate above the 4 ppb reporting limit in wells near the Aerojet site. Testing began on other wells throughout California, adjacent to sites that had known association with the use or manufacture of perchlorate-containing products. By January 1998, perchlorate had been detected in over 100 water supply wells in California and in Lake Mead and the Colorado River.

An increasing number of commercial and government laboratories have adopted the improved analytical method, leading to further discoveries of perchlorate contamination and an increase in monitoring water supplies. Development of a formal published method documenting the reproducibility and limitations of the technique is expected to facilitate the acceptance of perchlorate testing at low concentrations by laboratories across the country. The need for a reporting limit of 4 ppb taxes the sensitivity and reproducibility of the current IC method. A collaborative study of existing IC methods is planned for the near future. Work is also being planned to develop different analytical techniques to confirm the results of the IC method.

Monitoring water supplies and identifying possible sources of perchlorate contamination are not the only needs for analytical capability. A reliable and accurate method for analysis of perchlorate is essential for research in human health risk assessment, treatment technologies, and ecological toxicology. Results of these assessments may place additional requirements on analytical methods.

Characteristics of the Current Method

There are two components to perchlorate analysis, (1) separation of perchlorate from all other species in water, and (2) measurement of the separated perchlorate against suitable standards.

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Separation

Separation of perchlorate and other like dissolved species (anions) in water is based on the attraction (affinity) of perchlorate for a special organic exchanger (ion exchange resin) packed into a column for convenient use. The anions are carried through the column by a flow of solution (mobile phase or eluent). As the anions move through the column they separate into thin bands. Since the relative strength of the attraction of the different anions to the ion exchange resin is expected to be different for each dissolved specie, they separate and come off (elute from) the ion exchange column at different times. As the anions pass through the detector, the detector response is registered as peaks with a peak area or peak height proportional to concentration and at a retention time characteristic of the anion.

Detection

The separated bands of anions are detected by the electrical properties created by the combination of the mobile phase and anion in the detector at a given time. The property of the solution to conduct electrical charge is called the conductivity. A conductivity detector is able to detect and measure the subtle differences of solution conductivity and thereby measure the relative contribution of the anion of interest to the total conductivity.

Ideally, only the anion of interest would be present in the small volume of eluent containing the separated band of perchlorate while the eluent would be nonconducting, presenting the lowest background and highest sensitivity. Because the mobile phase is also conducting and adds to the overall background, the ideal situation can not be realized but something very close can be achieved. By removing (suppressing) the species in the mobile phase that contribute to the background but retaining the anion of interest by use of a special technique, conductivity, detection (sensitivity), and signal measurement can approach the ideal. This is the general approach used by most of the current IC methods.

Method Variations

Since the presence of perchlorate in various water supplies has become important, a number of method changes have been tried to increase the sensitivity of the IC method. The basic system components remain the same, an ion exchange column, eluent, some method of suppression, and conductivity detection. The hardware (pumps, tubing, materials of construction, the suppressor, and the detector) does not contribute directly to the chemistry of the separation. The chemistry of the eluent and the ion exchange resin seem the most promising variables to investigate at this time. Many laboratories and some commercial IC manufactures are presently engaged in this research and development.

Interferences

The elution time is the only parameter, at this time, that is used to determine if the peak can be presumed to be perchlorate. If other, yet unknown anions are also eluted at the same time as perchlorate, the IC method can not indicate the difference. If such were the case, the presence of and concentration of perchlorate would be unclear and a false positive would result with no method to further separate perchlorate from the interfering species. The common approach is to

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measure the elution times for other anions that might be present in water, alone and as mixtures with perchlorate. By a process of elimination it may be found that under a specified set of conditions perchlorate and only perchlorate will elute from the column. An attractive alternative is to develop a perchlorate-specific method which alone or in combination with IC would measure the concentration of perchlorate uninfluenced by any other chemical specie. This latter approach is a fertile, yet unexplored field of research and development.

Ongoing Actions and Next Steps

The analytical subcommittee of the Interagency Perchlorate Steering Committee (IPSC) is coordinating a collaborative study of the existing IC method and its variations. This method has been used to measure perchlorate in all water supplies where perchlorate has been tentatively identified. The subcommittee is composed of four scientists from EPA, the states of California and Utah, and the United States Air Force.

The referee facility is the EPA Office of Research and Development, Environmental Sciences Division, Environmental Chemistry Branch located in Las Vegas. The study design will evaluate the within laboratory precision (repeatability), between laboratory precision (reproducibility), method accuracy (bias), detection limit, and sensitivity. These are basic questions requiring an empirical (factual) solution. The results of this collaborative study will serve as a basis to focus future research and method development, with the overall goal to publish a standardized method or methods for low level perchlorate determination.

Questions for Discussion

Because the measurement of perchlorate will likely encompass other analytical strategies, the analytical subcommittee is interested in public comments on the following issue areas:

1. What are other IC technologies, if any? High pressure liquid chromatography, other anion exchanger not based on organic supports or modified surfaces?
2. What are other non IC technologies? Ion specific electrode, spectrophotometric methods, derivatization of perchlorate to facilitate detection by other techniques?
3. What are some possible analyte, perchlorate, specific method possibilities?
4. How do anions, such as chloride, fluoride, sulfate, sulfite, nitrate and nitrite, etc. and cations, such as sodium, potassium, and calcium commonly found in groundwater sources affect the ion chromatography, sensitivity, and specificity of perchlorate analysis?
5. Does the presence of organic solvent affect the ion chromatography, sensitivity and specificity of perchlorate analysis?
6. How stable is perchlorate in general, and with respect to light/dark storage conditions, container type, and the presence of other anions?

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PERCHLORATE CONTAMINATION IN THE ENVIRONMENT

Treatment Technologies

Introduction

Treatment technologies capable of removing perchlorate from water are urgently needed. Water utilities, in particular, need treatment methods that can reliably reduce perchlorate concentrations to low or non-detectable levels. Because the perchlorate ion is nonvolatile and highly soluble in water, it cannot be removed from water by conventional filtration, sedimentation, or air stripping. It appears to be only weakly removed by activated carbon. To be useful, a treatment method must be cost-effective, acceptable to regulatory agencies and the public, cause no other water quality problems, and minimize waste generation. The only option available for reducing perchlorate levels in contaminated water supplies is by blending uncontaminated supplies with those that containing perchlorate. In addition, the degree to which treatment options need to be developed is a function of the forthcoming results of the toxicology and health affects data and resulting peer reviewed reference dose for drinking water.

A few promising technologies are being developed for removal of perchlorate. Some are commonly used in water treatment, others less so. An anaerobic biochemical process has received the most attention, but reverse osmosis and ion exchange are also capable of removing perchlorate. Studies are underway to evaluate the cost, effectiveness, and implementability of these technologies.

The remainder of this fact sheet discusses the current state of perchlorate treatment technology, and current and planned treatment development efforts being carried out as part of U.S. Environmental Protection Agency (EPA) Superfund program studies, U.S. Air Force (USAF) research, water utility funded studies, and the federally funded research effort underway by the East Valley Water District, CA and the American Water Works Association Research Foundation (AWWARF). Technologies are grouped into three categories: physical, chemical, and biochemical.

Physical Processes (Ion Exchange, Reverse Osmosis, Nanofiltration)

There is no doubt that physical processes such as ion exchange and reverse osmosis can remove perchlorate from water. Of the two processes, ion exchange, in which the perchlorate ion is replaced by an innocuous anion (e.g., chloride), is currently receiving the most attention. Ion exchange technologies have not yet been used to remove low levels of perchlorate from drinking water supplies, but have been widely used in drinking water treatment to remove higher

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concentrations of nitrate, an anion similar to perchlorate. Perchlorate and nitrate are weakly hydrated in solution, and similar technologies are expected to be applicable to the treatment of both ions. In California's San Gabriel Valley, the Main San Gabriel Basin Watermaster is the primary sponsor of bench and pilot-scale tests of the performance of ion exchange technologies, with results expected by mid-1998. The San Gabriel Valley study is evaluating the cost and effectiveness of removing approximately 30 to 200 parts per billion (ppb) perchlorate from groundwater.

One current challenge is to find an ion exchange resin that can selectively remove perchlorate, thereby limiting the unnecessary removal of other ions which are typically present in far higher concentrations than perchlorate (e.g., chloride, sulfate, bicarbonate). Ion exchange processes (and reverse osmosis and nanofiltration) also generate perchlorate-rich waste brines that may be difficult to dispose. Further treatment of the brine may be needed to reduce its volume or toxicity before disposal.

Nanofiltration and reverse osmosis will also remove perchlorate, but at unknown cost. Pilot-scale tests completed by Harvey Mudd College for the Metropolitan Water District of Southern California have shown that nanofiltration can reduce perchlorate from 18 ppb to less than 4 ppb in a contaminated surface water supply, but at undetermined cost. In addition, the Southern Nevada Water Authority reportedly achieved satisfactory results in tests of in-home reverse osmosis units with trained operators.

Chemical Processes (Chemical Reduction, Ozone-Peroxide)

Perchlorate is a highly oxidized compound (i.e., it has a strong affinity for electrons). One might therefore expect that perchlorate could be destroyed by adding a chemical reducing agent to convert its chlorine atoms to chloride, a harmless component of table salt. Unfortunately, the chemical reaction between perchlorate and commonly used reducing agents is too slow to be of practical use. Perchlorate may react with more exotic reducing agents, such as titanium, vanadium, molybdenum, or ruthenium, but these chemicals are likely to be too unstable or toxic to be practical for water treatment. Catalysts that could selectively speed the destruction of perchlorate have not been identified.

Ozone-peroxide treatment appears to have minimal effect on perchlorate in water, but ozone-peroxide followed by liquid phase carbon treatment has been shown to remove perchlorate from groundwater at a water supply well in the San Gabriel Valley. EPA is planning additional tests to evaluate the long-term effectiveness, reliability, and cost of the process. AWWARF may also fund additional evaluations of this process as part of its \$2 million federally funded perchlorate treatment research program.

Biochemical Processes (Anaerobic Biochemical Reduction)

To date, more effort has been directed at developing an anaerobic biochemical reduction process than any other treatment option. In the biochemical reduction process, microbes are used to

convert perchlorate to a less toxic or innocuous form. Microbes have been used for decades in the treatment of some drinking water supplies, as part of a process known as slow sand filtration.

The Air Force Research Laboratory, Materials and Manufacturing Directorate began development of biochemical reactor systems for the treatment of high level perchlorate-contaminated wastewater, i.e. 1000 to 10,000 parts per million (ppm), more than eight years ago. A production-scale, continuous-stirred-tank-reactor system began treating wastewater from rocket motor production operations in Utah in 1997. Applying the same concept, pilot-scale tests of an anaerobic fluidized bed bioreactor were completed at the Aerojet Superfund site near Sacramento, California in 1996. The tests demonstrated that a bioreactor could reduce perchlorate concentrations in groundwater from over 5000 ppb to the low hundreds of ppb. A 4000-gallon per minute (gpm) flow-through bioreactor is expected to be online by late 1998 to treat contaminated groundwater before recharge to the aquifer.

Additional pilot-scale tests were recently completed by the Baldwin Park Operable Unit Steering Committee at one of the San Gabriel Valley Superfund sites, where groundwater contaminated with approximately 150 ppb perchlorate must be treated. Results from the San Gabriel Valley tests are encouraging; perchlorate has been reduced to nondetectable levels. The bioreactor also removed nitrate, which is present in the aquifer at 20 to 30 ppm (as NO₃). Larger-scale testing at 500 to 1000 gpm will continue later in 1998 at a perchlorate-contaminated drinking water supply well in the San Gabriel Valley. Ultimately, a perchlorate treatment facility with the capacity to treat 20,000 gpm is expected to be built with some or all of the treated water supplied to local drinking water utilities. Although bioreactors appear capable of removing low level perchlorate contamination from drinking water supplies, the cost, reliability, and public acceptance of this technology are not well established.

The Air Force Research Laboratory has also initiated an effort to isolate enzymes from the microorganism responsible for perchlorate reduction. If this effort is successful, enzymes might be used in a fixed-bed reactor system to selectively remove perchlorate over a range of concentrations.

Summary

Only in the last year has a substantial effort been directed at the development of perchlorate-removal technologies that could potentially be used to treat perchlorate-contaminated drinking water supplies. By late 1998 or early 1999, pilot-scale studies of two or three promising technologies will have been completed, and performance data from a full-scale anaerobic biochemical treatment system should be available. In 2001, results from the \$2 million AWWARF research effort will also become available.